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The Oxygen Index of Copolymer in Relation to its Composition

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Ethylene-propylene, ethylene-vinylacetate, ethylene-vinyl-alcohole, acrylonitrile-vinylacetate, and acrylonitrile-methyl-acrylate copolymers were investigated on their oxygen index(OI)-es in relation to their compositions.

The relationship between OI and composition of copolymer can be represented by the relationship between OI and heat of combustion (Ho, cal/g) of copolymer, as there is a linear relationship held between heat of combustion and composition of polymer.

The following equation is used to characterize the OI of the polymer in relation to the heat of combustion.
$[(m_p - m_o)OI + (0.044m_p + 0.956m_o) + 0.044m_o/OI]/0.0129MW = H_o$,
where m_p , m_o and MW are constants for each polymer.

Thermogravimetric and differential scanning calorimetric analyses were studied to explain the deviations of the observed OI values of the copolymers from the OI values calculated by averaging the OI values of their components.

1 Introduction

The oxygen indexes and the heats of combustion of the varius copolymers with the different compositions such as ethylene-propylene (Et-Pr), ethylene-vinylacetate (Et-VAC)[1)2)], acrylonitrile-methylacrylate (AN-MA) and acrylonitrile-vinylacetate (AN-VAC)[3)] have been reported as the values were obtained.

The OI values of AN-VAC, AN-MA, and Et-Pr copolymers are larger than those obtained by averaging the OI values of the components, whereas the OI values of Et-Pr copolymers do not exceed the OI values by averaging those of the components.

In this study, it was acertained at the beginning if a linear relationship held between Ho and component of copolymer or not. Then, the OI-Ho characteristic equation of polymer was applied to examine the OI values of the copolymers deviated from the calculated averages of the OI values of the components.

Results of the thermogravimetric and the differential scanning calorimetric analyses (TGA and DSC respectively) were also presented to study on the subject.

2 Experimental

2-1 Test materials. Et-VA copolymers (VA-66, VA-77) and Et-VAC copolymers (VAC-79, VAC-87) (Kuraray Co.). The same other

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co- and homo-polymers were used [1)2)3)].

2-2 Equipment and procedure. The apparatus and the test method for Ho or OI were the same as before mentioned.

TGA's were made on apparatus from Shinkuriko Co., TG-3000 with a heating rate 10°C/min on sample of 20 mg, using atmospheric air.

The sensibility was ± 20mg. DSC's were made on apparatus from Perkin-Elmer Co., DSC-1B Type, with a heating sample of 10 mg, using nitrogen atmosphere, with a heating rate 10°C/min.

3 Results and comments.

3-1 Relationship between Ho and composition of copolymer.

Fig. 1 shows the linear relationship held between Ho and composition of copolymer. From the result obtained, the relationship between OI and Ho of copolymer can be used to represent the relationship between Ho and composition of copolymer.

3-2 The OI-Ho characteristic equation of polymer.

As reported elsewhere[1)2)], between OI and Ho, an equation holds as follows.

$$OI = 0.0129\ Ho \cdot MW / (m_p + m_n) - 0.044 \qquad (1)$$

where m_o = moles of oxygen per mole of the constituent repeating unit of the polymer, for stoichiometric oxidation under the atmospheric condition of the OI test.

m_n = moles of nitrogen per m_o in the atmospheric oxygen index condition, $= m_o(1 - OI)/ OI$, $OI = m_o / (m_o + m_n)$.

m_p = moles of gaseous products in the flame atmosphere of the OI test. MW= molecular weight of the constituent repeating unit of polymer. Equation 1 can be developed as follows.

$$[(m_p - m_o)OI + (0.044m_p + 0.956m_o) + 0.044m_o/OI] / 0.0129MW = Ho \qquad (2)$$

By substituting the characteristic constants of m_o, m_p, and MW of each polymer in the above Equation 2, the resultant equations, listed in Table 1 for the homopolymers, Table 2 for the ethylene based copolymers, and Table 3 for the AN-copolymers, were obtained.

Per cent contribution of each term in Equation 2 to Ho is designed in the parentheses under the next column of the equation in Table 1.

The observed OI values and those of calculated from the observed Ho values by substituting them in Equation 1, their differences ΔOI, the Ho values obseved and those calculated from the observed OI values by substituting them in Equation 1, and their differences Δ Ho are listed in Tables 1~3 according to their classified positions.

Equation 2 has a shape of hyperbola where x-axis and a line represented by the formula , x = 1st term plus 2nd term of Equation 2

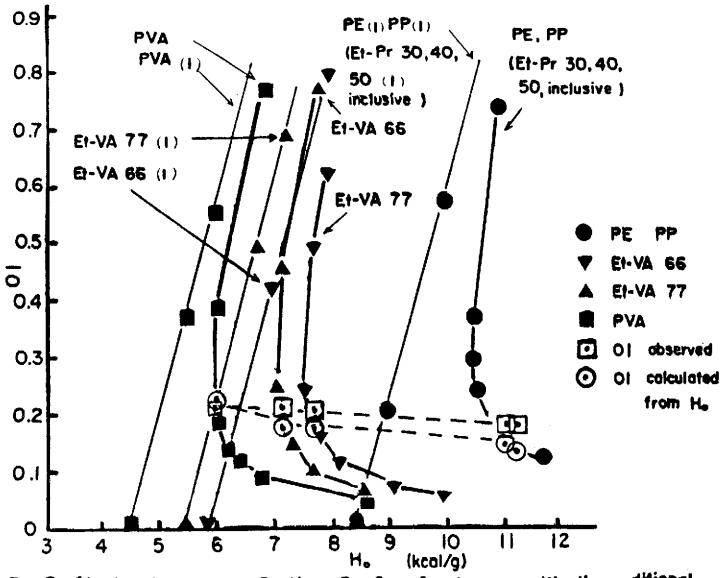

Fig. 2 OI - Ho Curves of Et-VA, Et-Pr Copolymers with the adtional analytical curves of OI - Ho Equations.

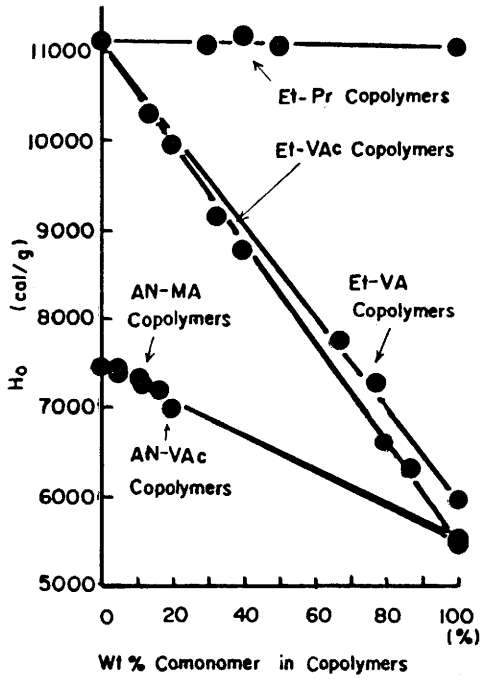

Fig. 1 Ho vs Wt % Comonomer in Copolymers

Table The OI-Ho Equations of Homo-Polymers and the Contributions of Each Term in the Equations on the Heat of Combustions.

Remarks; through Table 1 to Table 3
1st-term; $OI(m_p-m_0)/0.0129MW$,
2nd term; $(0.044m_p + 0.956m_0)/0.0129MW$,
3rd-term; $0.044m_0/0.0129MWOI$,
( ): Expressed in per cent based on Ho value.
differ : Difference between values observed and caluculated on OI and Ho.

mp : The exothermal peak Temperature observed by the DSC Analysis

Material	OI obs.	OI calc.	Ho (kcal/g)	OI(y)-Ho(x) Equations 1st- 2nd- 3rd-term	mp (°C)
PE	0.180	0.162	11101	2.769y + 8.429 + 0.365/y = x	125
	differ	0.018	0.111	(4.03) (75.75) (20.37)	
PP	0.180	0.176	11.027	2.769y + 8.428 + 0.366/y = x	160
	differ	0.004	0.037	(4.42) (76.43) (18.86)	
PS	0.185	0.162	9812	1.491y + 7.519 + 0.328/y = x	----
	differ	0.023	0.214	(2.46) (76.63) (20.63)	
Ny-6	0.259	0.224	7.423	2.573y + 5.773 + 0.249/y = x	----
	differ	0.035	0.061	(7.76) (77.77) (14.18)	
PMMA	0.175	0.187	6.301	2.326y + 4.753 + 0.2047/y= x	----
	differ	-0.012	-0.049	(6.91) (75.43) (17.37)	
PVA	0.225	0.230	5.989	2.643y + 4.521 + 0.194/y = x	229
	differ	-0.005	-0.006	(10.01) (75.42) (14.07)	
PVAc	0.202	0.196	5.526	2.254y + 4.154 + 0.178/y = x	37
	differ	0.006	0.015	(7.98) (75.19) (16.46)	
PMA	0.193	0.180	5.569	2.254y + 4.355 + 0.178/y = x	80
	differ	0.013	0.036	(7.86) (75.09) (16.70)	
PAN	0.202	0.153	7.448	1.828y + 5.565 + 0.241/y = x	280
	differ	0.049	0.296	(3.76) (74.71) (21.17)	
mean				6.65 75.82 17.84	
range				7.69 3.05 7.10	

Table 2 The OI-Ho Equations of Etylene based Co-Polymers and the Contributions of Each Term in the Equations on the Heat of Combustions.

Remarks;through Table 2 to Table 3, numerical figures cited just after material names :weight per cent.

*: Measured by the ordinaly H_2SO_4 method

Materials	OI obs.	OI calc.	Ho (kcal/g)	OI(y)-Ho(x) Equations 1st-, 2nd-, 3rd-term.	mp (°C)
Et-Pr Co-Polymers					
Pr-30 (Pr 22mol%)	0.175 differ	0.168 o.oo7	11.059 0.020	2.752y + 8.435 + 0.366/y = x (4.17) (76.16) (19.66)	105*
Pr-40 (Pr 33mol%)	0.175 differ	0.163 0.012	11.113 0.080	2.774y + 8.427 + 0.365/y = x (4.07) (75.78) (20.16)	85*
Pr-50 (Pr 40mol%)	0.175 differ	0.176 -0.001	11.026 -0.007	2.770y + 8.432 + 0.366/y = x (4.45) (77.16) (19.00)	80*
Et-VA Co-Polymer					
VA-66 (VA 55mol%)	0.206 differ	0.184 0.022	7.743 0.089	2.683y + 5.852 +).252/y = x (6.40) (75.83) (17.77)	166
VA-77 (VA 68mol%)	0.206 differ	0.186 0.020	7.186 0.067	2.669y + 5.415 + 0.233/y = x (6.93) (75.58) (17.49)	175
Et-VAc Co-Polymer					
VAc-14 (VAc4.8mol%)	0.202 differ	0.176 0.026	10.235 0.193	2.691y + 7.833 + 0.339/y = x (4.63) (76.53) (18.84)	85
VAc-20 (VAc6.8mol%)	0.202 differ	0.182 0.020	9.982 0.138	2.687y + 7.619 + 0.330/y = x (4.93) (76.70) (18.28)	80
VAc-33 (VAc14.6mol%)	0.219 differ	0.186 0.033	9.069 0.158	2.599y + 6.965 + 0.301/y = x (5.33) (74.80) (17.87)	45
VAc-40 (VAc17.8mol%)	0.219 differ	0.192 o.o27	8.732 0.114	2.559y + 6.730 + 0.291/y = x (6.31) (77.02) (17.35)	40
VAc-79 (VAc55mol%)	0.202 differ	0.189 0.013	6.676 0.062	2.360y + 5.052 + 0.218/y = x (6.68) (75.67) (17.28)	-
VAc-87 (VAc69mol%)	0.202 differ	0.183 o.024	6.278 0.094	2.320y + 4.710 + 0.203/y = x (6.76) (75.02) (17.67)	-

Table 3 The OI-Ho Equations of Acrylonitrile based Co-Polymers and the Contributions of Each Term in the Equations on the Heat of Combustions.

Materials	OI obs.	OI calc.	Ho (kcal/g)	OI(y)-Ho(x) Equations 1st-, 2nd-, 3rd-term.	mp (°C)
AN-VAc Co-Polymers					
VAc-4 (VAc 2.5mol%)	0.202	0.148	7.416	1.845y + 5.509 + 0.239/y = x	
	differ	0.054	0.331	(3.69) (74.49) (21.82)	247
VAc-12 (VAc 7.8mol%)	0.219	0.149	7.271	1.879y + 5.395 + 0.234/y = x	
	differ	0.070	0.375	(3.86) (74.49) (21.66)	247
VAc-19 (VAc12.8mol%)	0.219	0.164	7.032	1.908y + 5.298 + 0.229/y = x	
	differ	o.o55	0.347	(4.46) (75.58) (19.96)	234
AN-MA Co-Polymers					
MA- 4 (MA2.8mol%)	0.219	0.148	7.395	1.845y + 5.509 + 0.239/y = x	
	differ	0.071	0.395	(3.69) (74.49) (.21.82)	258
MA-11 (MA7.8mol%)	0.219	0.148	7.270	1.879y + 5.409 + 0.234/y = x	
	differ	0.071	0.385	(3.89) (74.40) (21.18)	257
MA-16 (MA10mol%)	0.228	0.154	7.134	1.896y + 5.340 + 0.231/y = x	
	differ	0.074	0.354	(4.09) (74.86) (21.05)	220

Table 5 Results of Thermo-Gravimetric Analysis of Polymers.

Remarks;
m.p. : Exothermal Peak Temperature observed by the analysis of DSC method.

Materials	Decomposition Temp. (°c)	Wt. Loss (%)	Char Residue at 500°C (%)	Char Residue at 600°C (%)	Temp. of Half Wt. (°c)	m.p. (°c)
AN-VAc Co-Polymers						
VAc- 4	303-365	23	40	57	690	247
VAc-12	295-365	35	43	56	700	247
VAc-19	290-428	34	43	57	693	234
AN-MA Co-Polymers						
MA- 4	305-340	26	42	49	589	258
MA-11	300-428	33	43	47	570	257
MA-16	290-430	39	44	48	581	220
PAN	306-340	26	37	58	741	280

form its asymptotes, when Ho and OI are plotted as x and y respectively. The means and ranges (maxium and minimum) of the numbers in the parentheses of each term are calculated and the results are listed in Table 1.

Contribution of the 2nd term to Ho. Although the 2nd term of Equation 2 does not include OI term, 75.8% of contribution to the overall Ho value is computed, having the range as small as 3.05%.

We have reported already that a linear relationship held between m_o and Ho as follows[1)2)].

$$Ho = 744 + 92605\ m_o/MW \qquad (3)$$

Equation 3 has the mean Δ Ho = 230 cal/g, which is comparatively small (sample size = 15).

Contribution of the 3rd term to Ho. Johnson has proposed the following equation, with some exceptions such as PAN, polyester, cotton, etc., $OI = 1.9 / Ho$[4)].

The contribution of the 3rd term is 17.84% to the overall Ho. The range is 7.10% (ca 40% based on 17.84%).

Contribution of the 1st term to Ho. The amount of the contribution is 6.65%. The range is 7.69%. The 1st term is a fraction where OI term is proportional to Ho. The sum of the 1st and 2nd terms is 24.29%. The range is as small as 3.06%.

Et-Pr copolymer. The coefficient of the each characteristic equation of the Et-Pr copolymers and their component homopolymers are substancialy the same. The observed OI values of the copolymers locate on a little bit lower parts of the same hyperbola than the positions of the OI values of the components, where x-axis and $x = 2.77y + 8.43$ are the asymptotes.

Et-VA copolymer. The two kinds of the copolymers tested have $\Delta OI = 0.2$ and 2.2%. ΔOI of PE and PVA are 1.8% and -0.5% respectively. The difference of the coefficients of the 1st terms of the both PE and PP equations are only 0.126 and the asymptotes are practicaly parallel to each other, as shown in Fig. 2.

Fig. 2 illustrates the OI (y) and Ho (x) curves of Et-Pr and Et-VA copolymers. Not only in Fig. 2, but also in Fig. 3 and 4, suffix 1 represents a line expressed by x = the 1st term plus the 2nd term of Equation 2. The observed OI values plotted in Fig. 2 show nearly straight. If any two characteristic equations of Et-VA copolymers and their components inclusive are choised and distinguish them by giving suffix i and j, the following relationship holds practicaly.

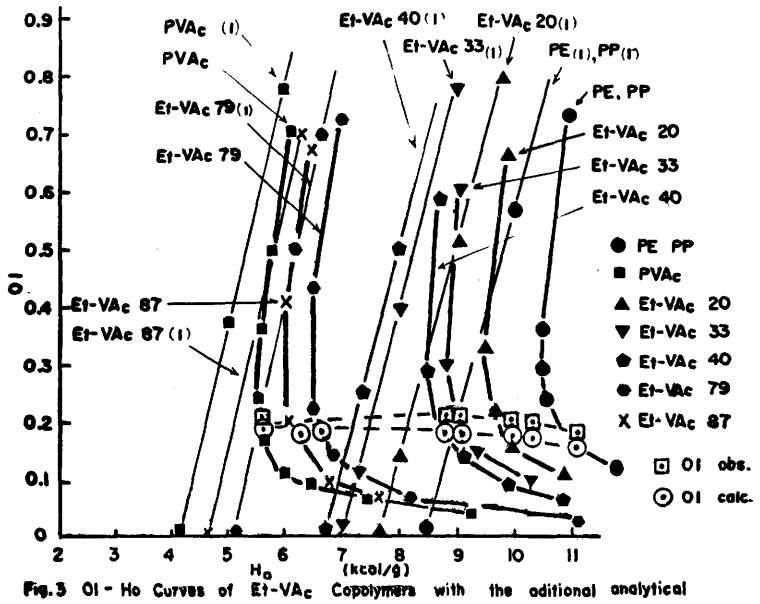

Fig. 3 OI - Ho Curves of Et-VAc Copolymers with the aditional analytical curves of OI - Ho Equations.

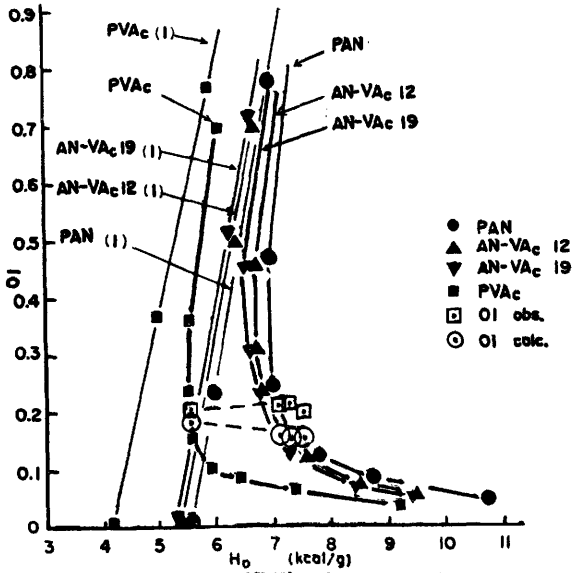

Fig. 4 OI - Ho Curves of AN-VAc Copolymers with the aditional analytical curves of OI - Ho Equations.

(the 2nd term i)/ (the 2nd term j) = (the 3rd term i) / (the 3rd term j). (4)

Et-VAC copolymer. They have Δ OI = 1.3~3.3%. These values are larger than that of PVAC of 0.6%.

Fig. 3 shows a convex curve of the observed OI. The magnitude of the coefficient of each term of PE characteristic equation in Table 1 shows larger value than that of PVAC. The coefficient of copolymer has the smaller value as the VAC content in composition decreases, as shown in Table 2. Equation 4 does not hold here.

AN-VAC and AN-MA copolymers. Fig. 4 shows the relation between OI and Ho. A covex curve of AN-VAC copolymers is drawn on the observed OI values. Contrary to Et-VAC copolymers, the coefficients of the 1st terms of AN-copolymers get larger values as the VAC or MA content increases in the composition of copolymer.

AN-VAC and AN-MA copolymers have Δ OI =5.4 ~ 7.0% and 7.1~7.4% respectively. These values are much larger than that of PAN which has Δ OI = 4.9%.

Et-VAC and AN-copolymers, which have larger ΔOI values than that of PVAC or PAN, have their OI curves of convex tendencies, whereas Et-Pr or Et-VA coplymers, which forms a curve of rather straight or a little bit concave tendency, has the small Δ OI value as that of PE. It has been pointed out that ΔOI of PAN was anomalous.

3-2 Results of TGA and DSC.

The burning process proceeds in several stages: softening and melting of polymer → pyrolysis, generation of flammable gas → flash or self ignition → flame propagation.

OI measurement procedure deals with the last stage, whereas TGA corresponds to the first two stages.

Fig 5~8 show the results of TGA curves obtained.

It is observed that the TGA curves of Et-Pr copolymers shift to the lower temperature-side than that of PE or PP.

The larger part of thermal decomposition of the copolymers seem to proceed at the lower temperature-side than that of the component homopolymers.

This fact shows a possibility of the existance of the lower OI values of Et-Pr copolymers other than the OI valued calculated by weight averaging the OI values of PE and PP.

Et-VA copolymers show the analogous TGA curves as PVA, as VA component are rich in composition , but the Et-VA copolymers show the larger decreasing rate of decomposition than that of PVA.

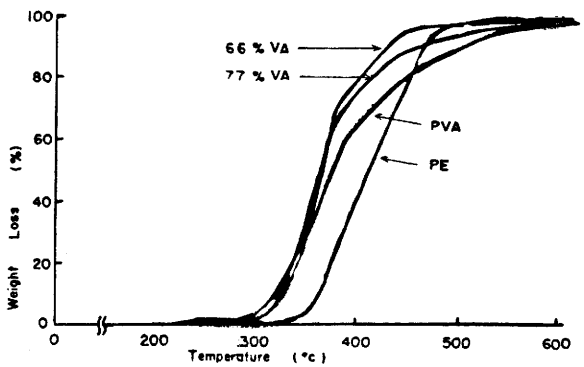

Fig. 6 TGA curves of Et-VA Copolymers.

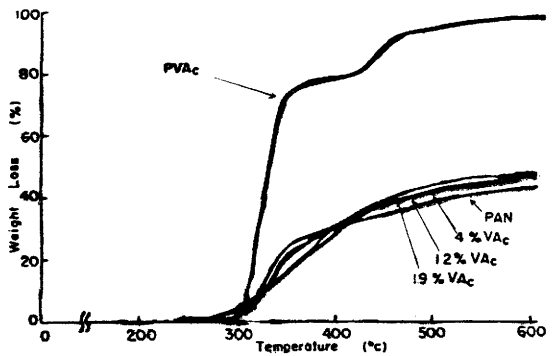

Fig.8. TGA curves of AN-VAc Copolymers.

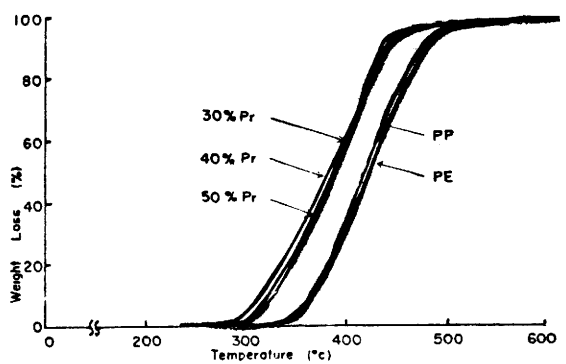

Fig.5 TGA curves of Et-Pr Copolymers.

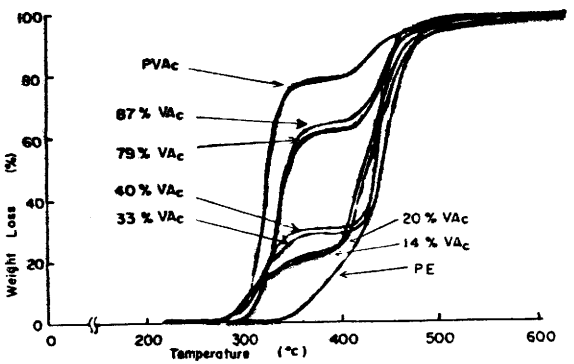

Fig. 7 TGA curves of Et-VAc Copolymers.

Table 4 Results of Thermo-Gravimetric Analisis of Polymers.

Remarks;
m.p. : Exothermal Peak Temperature observed by the analysis of DSC method.

Materials	First-Stage Temp. (°c)	First-Stage Wt. Loss (%)	Second-Stage Temp. (°c)	Second-Stage Wt. Loss (%)	resi-dual Solid (%)	Char resi-due at 600°c (%)	Temp. of Half Wt. (°c)	m.p. (°c)
Et-Pr Co-Polymers								
Pr-30	292-443	94	-	-	6	2	397	105
Pr-40	313-446	92	-	-	8	4	406	85
Pr-50	319-438	95	-	-	5	2	394	80
Et-VA Co-Polymers								
VA-66	332-385	71	385-454	26	3	1	371	166
VA-77	323-373	64	373-433	25	11	1	362	175
Et-VAc Co-Polymers								
VAc-14	297-364	21	397-448	61	10	5	423	85
VAc-20	292-361	21	395-464	61	8	3	421	80
VAc-33	290-350	28	423-450	64	8	5	434	45
VAc-40	305-345	30	426-456	65	5	3	440	40
VAc-79	304-359	61	416-457	32	7	4	348	-
VAc-87	304-353	69	414-458	24	7	4	345	-
PE	358-467	97	-	-	3	1	440	125
PP	356-453	94	-	-	6	5	414	160
PVA	315-374	55	374-432	28	17	3	368	229
PVAc	306-339	75	408-426	12	13	3	328	37
PMA	328-390	82	-	-	18	4	369	80

Comparing the ranges of the decomposition temperatures of the Et-VAC copolymers to that of PVAC, the TGA curve of PVAC shows rapid weight loss up to 75% at the 1st decomposition stage, followed by the slow decomposing 2nd stage, whereas in the case of the Et-VAC (14~40) copolymers, after recording up to 20~30% of the rapid loss at the 1st stage, slow decomposing stage appear rather promptly. This may be one of the causes that the OI curve of the Et-VAC copolymers have maximum.

The shapes of the TGA curves of AN-copolymers and PAN are similar and can not signify their differences clearly.

If the rates of the decompositions are equal to each other, the rate of melt fusion will dominate the flame propagation such that OI value will increase as melt and drip rate increase.

The exothermal peak temperature of PAN measured by DSC is 280°C whereas the AN-MA and AN-VAC copolymers have their peak temperatures = 220~258°C and 234~247°C respectively.

One of the reasons, that the OI values of AN-copolymers have larger OI values than the values calculated by averaging the OI values of the components, may be the decrease of the peak temperatures which are assumed to be the melting points of polymers, other conditions assumed to be the same. Table 4 and 5 show the results of TGA and DSC.

Acknowledgement

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Literature Cited

1) Hideo Ohe and Koichi Matsuura, Nippon Kagaku Kaishi, NO. 10, 1813 (1975)

2) Ditto, Textile Res. J., 45, 778 (1975); Memoirs of the Faculty of Engineering, Fukui University, 23, 165 (1975, No.2)

3) Hideo Ohe, Koichi Matsuura, Naoto Sakai, reported on Oct. 23, (1975) at the 7th Fiber Union Research Congress, in press.

4) P.R. Johnson, J. Appl. Polym. Sci., 18 , 491 (1974)

5) D.O. Douglas, J. Soc. Dyers. Col., 73, 258 (1957)